certain tar oils, especially where the use of chemicals would become too costly.

9. *Formation of Resins and Asphalt from Primary Tar by Oxidation under Pressure*

If oxidation under pressure is continued for several hours, the bulk of the oil is eventually converted into a solid black mass of unknown composition. The formation of resinic and asphaltic solids has been studied in the case of primary tar from bituminous coal both with tar and tar oils,[137] and separately with hydrocarbons and phenols.[138] Phenols pass even more rapidly than hydrocarbons into a solid resinic or asphaltic mass, brown when finely divided and black when fused, which on prolonged oxidation becomes insoluble in all solvents. The liquid hydrocarbons differ somewhat from phenols in this respect, their conversion into similar products being slower and not complete. The solid paraffins of primary tars have been studied more fully; [139] by oxidation under pressure they are converted into higher fatty acids, suitable for soap manufacture and other purposes.

10. *Fatty Acids from Crude Paraffin Wax by Oxidation under Pressure*

The higher fractions of primary tar contain paraffin wax together with viscous oils. Their relative proportions vary within wide limits. In products poor in paraffin wax, which are liquid at ordinary temperature, its presence is indicated only by the high setting point; the corresponding fractions of tar from the carbonisation of brown coal are quite congealed owing to their higher paraffin content. It has been found that crude paraffin wax from primary tar, freed of viscous oils in hydraulic presses, can be converted into fatty acids by oxidation under pressure of air at 170° in the presence of soda lye. Soaps have been prepared in this way in the laboratory.[139] This brief consideration of the oxidation of primary tar and tar oils may suffice for the present purpose.

(*s*) CONVERSION OF LOW-TEMPERATURE CARBONISATION TAR INTO COKE-OVEN TAR

Although this book is intended to deal only with recent processes for the production of oils from coal, and not with the by-products industry of gas works and coke-ovens, which already yield very considerable quantities of liquid fuels, benzol, etc., it appears appropriate to refer to the conversion of low-temperature tar into coke-oven tar in connection with the chapter on the thermal treatment of primary tar. Fractions of coal tar poor in hydrogen (naphthalene) are already being liquefied by hydrogenation, and thus rendered more suitable for power purposes.

Berthelot's old " acetylene hypothesis," which held the field for a long time, explained the formation of the aromatic constituents of coal tar by the primary generation of acetylene in the retort, and the subsequent polymerisation of acetylene into benzene ($3C_2H_2 = 3C_6H_6$) and its derivatives. A discussion of this hypothesis is hardly called for any more; it has been discarded, in the first instance because the temperatures in the coke-oven or gas-retort are not sufficiently high to lead to an appreciable formation of acetylene, and further because Amé Pictet [7] showed that vacuum tar from coal, a preliminary stage in the formation of low-temperature tar, can be easily converted into an ordinary coal tar by superheating. Pictet passed vacuum tar vapours through an iron pipe heated to a bright red heat which was filled with small pieces of coke. He obtained from 150 to 200 litres of gas per kg. of vacuum tar which had the smell of coal tar, and consisted essentially of hydrogen and saturated hydrocarbons of the methane series with a small proportion of ethylene. The resulting tar smelled like ordinary coal tar; the presence of benzene, naphthalene and anthracene was easily established. This was definite proof that the well-known constituents of coal tar are secondary, and not direct, products of the destructive distillation of coal.

D. T. Jones [140] concluded from his investigations that the formation of coal tar from vacuum tar was essentially due to the decomposition of the naphthenes, paraffins and unsaturated hydrocarbons forming olefines of various carbon content which condense at higher temperature to aromatic substances. Jones observed that the higher (gaseous) olefines are at a maximum at 550°, the curve descending to a minimum at 750°, when they virtually disappear. Their disappearance at 750° synchronises with the appearance of naphthalene, and immediately precedes a rapid increase in the evolution of hydrogen. Hydrogen is formed at middle temperatures, chiefly as the result of the decomposition of naphthenes. The increase at higher temperature must probably be attributed to the union of aromatic molecules and to intramolecular ring-closing. Jones further suggests that benzene and its homologues are chiefly formed as the result of olefinic condensation. To some extent they are secondary products of coal distillation, having been formed by the thermal dehydrogenation of the corresponding naphthenes.

The latter suggestion of Jones may be accepted unconditionally. That the bulk of benzene and its homologues has been formed in another way, *i.e.*, by the reduction of phenols, has meanwhile been established by other investigators.[141] Although the conditions prevailing in the coke-oven are not as favourable as those in the tinned iron tube (see p. 117) for a quantitative reduction of the phenols, they are sufficiently so to explain the formation of all benzene usually produced in practice. For it has been shown that as much as half or one-third of the theoretical benzene yield can be obtained when the reduction takes place under the most unfavourable conditions. The deposition of carbon observed in this case takes place also in the coke-oven, and part of this carbon is found in the tar.

All intermediate stages between primary tar and high-temperature tar are occasionally met with in industrial practice. The liability of primary tar to change, even at 300°, is shown in ordinary distillation, when the most viscous constituents are decomposed into light oils, gas and coke. That these constituents can be isolated at all in the distillation of coal is due to their being diluted by other more stable volatile compounds, and above all to their rapid discharge from the retort or rotating drum. Duration of the reaction and dilution exert an important influence upon the course of the reaction at a given temperature. The dehydrogenation of hydro-aromatic constituents and cracking probably begin at about 500°. The reduction of phenols to benzene and its homologues does not set in below 700°; any benzene hydrocarbons produced at lower temperature are therefore of different origin. A study of the products which have not yet appeared at 500°, and which disappear again at very high temperatures, should prove full of interest. The appearance of carbolic acid and acetone, which are not present in normal primary tar, is probably a case in point.

As has been shown in a previous section, a primary tar, not superheated, contains only a negligible quantity of carbolic acid. Phenol itself, therefore, cannot be the only source of the much larger quantity of benzene in coal tar, which, as has actually been proved, is chiefly derived from cresols and xylenols by simultaneous reduction and demethylation with the formation of water and methane. The term " simultaneous " should not be taken too literally. It would appear that toluene is formed more readily from cresols, and benzene secondarily from toluene. The benzene resulting from this reduction frequently contains 20 per cent. of toluene, whilst a benzene containing appreciable quantities of carbolic acid has never been observed, which should be the case if carbolic acid were first produced by demethylation, and benzene afterwards by reduction. It may be possible to select conditions in which demethylation takes place in the first instance, which would be important for the production of carbolic acid.

If we assume the reduction of xylenol to xylene to be completed, the further action of hydrogen would, according to present views, lead to the formation of toluene and methane. The formation of benzene would then follow with renewed evolution of methane. It has been shown [142] that toluene, at high temperature and in the absence of hydrogen, will split off hydrogen and then pass into larger molecules of dibenzyl, stilbene, ditolyl and *p*-methyldiphenylmethane, as indicated below.

$$2C_6H_5{\cdot}CH_3 \left\{ \begin{array}{l} = CH_3{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CH_3 + H_2 \\ = C_6H_5{\cdot}CH{:}CH{\cdot}C_6H_5 + 2H_2 \\ = C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5 + H_2 \\ = C_6H_5{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_3 + H_2 \end{array} \right.$$

In the case of benzene, the reaction $2C_6H_6 \rightleftharpoons C_6H_5{\cdot}C_6H_5 + H_2$ proceeds similarly, from left to right when there is a deficiency of hydrogen, and from right to left when hydrogen is in excess. The formation from phenol of a large number of solid compounds in coal tar can thus be explained, but that of naphthalene is not yet certain. Part of the naphthalene in coal tar is no doubt formed from methyl-naphthalene, or by simultaneous dehydrogenation and demethylation of the hydrogenated methyl-naphthalenes of primary tar. Another portion is probably of thermal origin, and must be considered as a very stable final product of condensation and dehydrogenation processes acting on benzene and its homologues, as must also be anthracene.

(*t*) CONVERSION OF BROWN COAL TAR INTO AROMATIC TAR

So far as can be judged at present, the primary tars from brown coal and bituminous coal differ mainly in the proportions of the various types of constituents. The Montan wax of brown coal consists of waxes and resins. The composition of the waxes is fairly well understood. They consist of the esters of higher fatty acids (C_{25},C_{27},C_{29}) [143] with high alcohols (C_{24},C_{26},C_{30}),[144] and of an excess of free fatty acid of high molecular weight. Whilst the fatty acids in the carbonisation of brown coal are converted via ketones into the corresponding paraffins, carbon dioxide being split off, the alcohols conceivably form olefines with liberation of water, or naphthenes by the closing of rings. Primary brown coal tar also contains phenols, largely derived from ulmins, the main constituents of coal. In brown coals rich in wax, the ulmic constituents are relatively less predominant; tar from such coals, therefore, contains more decomposition products of Montan wax and less phenols. In general, a tar from rich brown coal differs from that of good bituminous coal by its high content of paraffin wax and its low percentage of phenolic components.

The liability of primary brown coal tar to decomposition in ordinary distillation, and its behaviour on cracking under pressure, have been mentioned before. Its behaviour at about 700° was investigated by Liebermann and Burg [114] as early as 1878. It was then found that the fractions 200° to 300° of a brown coal tar oil, mainly consisting of hydrocarbons, contained only 4 per cent. of benzene after passage of the oil through an iron tube charged with pieces of wood charcoal at bright red heat. In explanation, Salzmann and Wichelhaus [115] suggested that, in the formation of products richer in carbon and poorer in hydrogen than the raw material, the vapours took up carbon from the incandescent charcoal, or that hydrogen was liberated, or that the molecules of vapour were dissociated into molecules of high and of low hydrogen percentages, benzene being one of the latter products. To-day we know that none of the three assumptions can be maintained, but that the bulk of benzene is a reduction product of phenol. A primitive conversion of brown coal tar oils into coal tar-like products has thus long been known, but by selecting working conditions with present-day knowledge much better results should now be realisable, as they are in the case of the hydrogenation of petroleum (*Brennstoff-Chemie*, 1923, 4, 201).

(*u*) LIQUID MOTOR FUELS BY HYDROGENATION OF COAL TAR, AND ESPECIALLY OF NAPHTHALENE

Modern methods applied in gas works and in coke-oven plants have become more and more alike. In recognition of the fact that the production of a good coke is of great economic importance, a number of gas works have even been fitted out with coke-oven plant. The manufacture of a firm coke calls generally for rapid heating by plunging the coal into incandescent chambers. Primary tar is not obtainable under these conditions; in its place appears coke-oven or gas tar in much smaller quantity and with a naphthalene content increasing with the temperature used. Owing to its ready crystallisation, naphthalene is one of the few products of coal tar which can be easily isolated and purified by pressing, recrystallisation and sublimation. Its annual production is very considerable, and its suitable utilisation has long been a problem of some importance. At one period naphthalene was used as a cheap motor fuel. One of the drawbacks attaching to its use was that it had to be melted and fed into the engine through heated pipes. It was, therefore, desirable to convert the solid naphthalene into a liquid fuel. It was found that purified naphthalene on heating in an autoclave with 4 per cent. of aluminium chloride at a pressure of 10 atm. undergoes, in less than half an hour, a change, so that it yields from 30 to 40 per cent. of a liquid product.[145] The aluminium chloride seems to act in this reaction as a hydrogen carrier, one part being hydrogenated, and another dehydrogenated and condensed. The reaction may be expressed by the equation :—

$$3C_{10}H_8 = C_{10}H_7 \cdot C_{10}H_7 + C_{10}H_{10},$$

the products being di-naphthyl and di-hydronaphthalene. The liberation and addition of hydrogen is, however, not limited to the formation of these two products, but leads to derivatives either richer or poorer in hydrogen. Partial liquefaction of naphthalene was superseded by the tetralin process.

Sabatier and Senderens had shown that naphthalene vapour passed over finely divided nickel at 200°, in the presence of an excess of hydrogen, is transformed into tetra-hydronaphthalene (b. p. 205°). At 175°, deca-hydronaphthalene (b. p. 187°) is the hydrogenated product (Sabatier, "Catalysis"). Schroeter[146] modified the process on the lines of the fat-hardening method by working with the liquid material and hydrogen under pressure, in the presence of nickel. The technical application of this obvious proposal was rendered very difficult by the sulphur compounds in commercial naphthalene, which rapidly poison the catalyst. Those difficulties were eventually overcome by a preliminary purification. The elimination of the last traces of sulphur by means of sodium, and the reduction of the sodium consumption to economic limits, made manufacture on a very large scale possible.

To-day, according to this method, a number of other hydrogenated products are manufactured on a large scale at suitable temperatures and hydrogen pressures, among these being tetra-hydronaphthalene (tetralin), deca-hydronaphthalene (decalin) and various derivatives of benzene, phenol and their homologues.

That a purification by the aid of sodium, and consequently the catalytic hydrogenation with nickel as catalyst, is commercially impracticable in the case of tar and tar oils has already been stated. These materials may be submitted to Berginisation. The following is an extract from the Patent Specification dealing with this invention.

Bergius' Brit. Pat. No. 5021 *of* 31 *March,* 1915 (*date of application in Germany,* 2 *April,* 1914)

"This invention is an improvement in or modification of that described in Specification No. 18,232 of 1914. In carrying out the process according to the prior specification with pressures of more than 20 atmospheres, it has been found that the hydrogenating reaction can be effected not only with coal and other solid carbonaceous material of vegetable origin, formed by natural or artificial carbonisation, but with certain products of distillation of coal and of the said other carbonaceous materials, such as tar and pitch and other solid or liquid carbon compound obtained by distillation. It is possible to convert tar by heating it with compressed hydrogen of more than 20 atmospheres to temperatures of about 400° C. into a fairly thin fluid, from which hydrocarbons having properties similar to those of rock oil hydrocarbons can be separated by distillation.

"The process is applicable to solid and liquid hydrocarbon containing products of destructive distillation of coal and other solid carbonaceous material of vegetable origin formed by natural or artificial carbonisation, obtained at high temperatures in coking and gas retorts.

EXAMPLE

"One kg. of tar is heated with hydrogen at 100 atmospheres pressure to 400° C. in an autoclave. After 4 hours, the mass is distilled off. Sixty per cent. of tar is distilled at about 250° C. and can be further treated by rectification.

"Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

"A process of manufacturing liquid organic compounds as set forth in Specification No. 18,232 of 1914, applied to the solid or liquid products of destructive distillation at the high temperatures of coking and gas retorts of coal or other substances produced by natural or artificial carbonisation of vegetable matter and carried through at pressures of more than 20 atmospheres."

The following details of an experiment of this kind may be quoted.[147] Gas works coal tar was freed of its constituents boiling below 230°. It was then charged into an autoclave together with its own weight of pebbles and 5 per cent. of iron oxide; hydrogen was forced in under pressure of 50 atm., and the contents were stirred. The temperature was raised to 480°, and then kept constant until there was no further drop of pressure. After cooling, the pressure was 32 atm. It was raised again to 50 atm. by replenishing the hydrogen, and heating to 480° was repeated until the pressure reduction had ceased once more. After cooling, a gas pressure of 30 atm. was observed. There had thus been a total pressure loss of $18 + 11 = 29$ atm., which would, in the autoclave of 5 litres capacity, correspond to a consumption of $4{\cdot}4 \times 29 = 128$ litres of hydrogen, making due allowance for the volume of the charge. The density of the tar, originally 1·144 at 15°, had been reduced by hydrogenation to 1·041; 33 per cent. of the reaction product boiled below 230°, and another 33 per cent. between 230° and 330°.

Part of the combined carbon of the original tar was, after the experiment, in the gas, of which 140 litres were blown off. It contained only 48 per cent. of hydrogen, and 39·6 per cent. of methane and its homologues. That would mean a certain loss, but the gas can be readily used like ordinary coal gas, being similar in composition. The original tar had an ultimate composition: carbon 87·56 per cent., hydrogen 6·04 per cent.; the composition of the Berginised product was :—

	Carbon.	Hydrogen.
Fraction below 170° . . .	83·48%	11·26%
,, 170–230° . . .	85·09%	8·56%
,, 230–330° . . .	88·98%	7·31%

The figures prove that, in the hydrogenation of tar oils, Berginisation can indeed replace the tetralin process which cannot be applied to these for obtaining products of lower boiling points from higher-boiling compounds. In view of the high temperature of 480°, hydrogenation, presumably, cannot be pushed above certain limits, unless pressures of several hundred atmospheres are available. It has been shown that the Berginisation of primary brown coal tar does not give larger yields of benzine than cracking under pressure and without hydrogen. This may be explained by the fact that the material treated was much richer in hydrogen than gas works' tar, and that, for this reason, hydrogenation soon came to a standstill. That view would dispose of the apparent contradiction in the facts that hydrogenation of the high-boiling fractions of gas works' tar was successful, whilst the same process did not, as regards yields of low-boiling constituents, offer any advantage over cracking under pressure when applied to brown coal tar, though it yielded better and less unsaturated products. This argument is supported by Waterman's experiments with paraffin wax.

(v) Importance of Primary Tar as Raw Material

In concluding the principal chapter of this book, which was devoted to the production of primary tar, with a discussion of its working-up, I should like briefly to give my reasons for the importance which I attach to the production of primary tar and to the knowledge at least of some classes of the bodies * contained in it. Primary tar must be regarded as a raw material, and not as a finished product of manufacture. By selection and invention of suitable methods it can be worked-up into valuable products, light and heavy liquid fuel and lubricants. By appropriate thermal treatment, primary tar, if it does not contain products utilisable in the chemical industry, will give the known coal tar products in higher purity and better yield, because the temperature of decomposition can be controlled at will and is not fixed by the requirements of the coke-oven or gas retort. Systematic thermal treatment of primary tar is bound to produce results of value to the chemical industry, as is indicated by the formation of carbolic acid and acetone under certain conditions.

For those reasons it appears perfectly justifiable to recover from coal before it is used for other purposes the most primary kind of tar which at the same time represents the highest possible yield.

The residue of carbonisation is, by one of the most interesting modes of application, converted into Synthol (Chapter IV); water gas is made from semi-coke and subsequently transformed into motor fuel by a contact process on the lines of Haber's ammonia synthesis. Primary tar treatment which yields chiefly heavy fuels, and the Synthol process which converts the semi-coke into light fuels, would supplement one another in a most fortunate sequence of manufactures, leaving behind nothing but the mineral constituents of coal.

* The isolation of individual compounds is of no value for the knowledge of primary tar, as long as their quantitative relationship is not definitely known and if there is no definite proof that the product examined is in fact a primary tar and not a product of superheating it.